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Ionic complexes simultaneously containing fullerene anions and coordination structures of metal phthalocyanines with I^- and EtS^- anions

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The ionic complexes simultaneously containing negatively charged coordination structures of metal phthalocyanines and fullerene anions, *viz.*, $\{Mn^{II}Pc(CH_3CH_2S^-)_x \cdot (I^-)_{1-x}\} \cdot (C_{60}{}^{\bullet -}) \cdot (PMDAE^+)_2 \cdot C_6H_4Cl_2$ (PMDAE is *N,N,N′,N′,N′*-pentamethyldiaminoethane, $x = 0.87$, **1**) and $\{Zn^{II}Pc(CH_3CH_2S^-)_y \cdot (I^-)_{1-y}\}_2 \cdot (C_{60}{}^-)_2 \cdot (PMDAE^+)_4 \cdot (C_6H_4Cl_2)$ ($y = 0.5$, **2**) were synthesized. The both compounds were obtained as single crystals, which made it possible to study their crystal structures. In complex **1**, the fullerene radical anions form honeycomb-like layers in which each fullerene has three neighbors with center-to-center interfullerene distances of 10.13—10.29 Å. Rather long distances between the $C_{60}{}^{\bullet -}$ radical anions results in the retention of monomeric $C_{60}{}^{\bullet -}$ in this complex down to the temperature of 110(2) K. In complex **2**, fullerenes form dimers $(C_{60}{}^-)_2$ bonded by one C—C bond. The dimers are packed in corrugated honeycomb-like layers with interfullerene center-to-center distances of 9.90—10.11 Å. Manganese(II) and zinc(II) phthalocyanines coordinate iodide and ethanethiolate anions to the central metal atom to form unusual negatively charged coordination structures $M^{II}Pc(An^-)$ (An^- is anion) packed in dimers $\{M^{II}Pc(An^-)\}_2$ with a short distance between the phthalocyanine planes (3.14 Å in **1** and 3.27 Å in **2**). The pthalocyanine dimers also form layers with the $PMDAE^+$ cations, and these layers alternate with the fullerene layers. The packing of spherical fullerenes with planar phthalocyanine molecules is attained by the insertion of fullerenes between the phenylene groups of phthalocyanines. The π—π-interactions of the porphyrin macrocycle with five- or six-membered fullerene rings are characteristic of the earlier studied ionic porphyrin and fullerene complexes. Such interactions are not observed for ionic complexes **1** and **2**.

Key words: fullerene C_{60}, manganese(II) and zinc(II) phthalocyanines, crystal structure, dimerization of $C_{60}{}^{\bullet -}$, coordination of anions with metal phthalocyanines.

Considerable interest given presently to the synthesis and study of the fullerene complexes with metal porphyrins is due to promising photophysical properties of these complexes[1] and wide possibilities of obtaining crystals of metal porphyrin complexes with endometallofullerenes, higher fullerenes, and chemically modified fulleneres, which makes it possible to study their molecular structures.[2—5] Ionic complexes of fullerenes with metal porphyrins can exhibit high conductivity and magnetic spin ordering.[6] The synthesis of these compounds allows one to study the structures and properties of negatively charged fullerenes in them. The ionic fullerene complexes with metal porphyrins have been synthesized for the first time with chromium tetraphenylporphyrinate ($Cr^{II}TPP$) and tin tetratolylporphyrinate ($Sn^{II}TTolP$), which are strong donors capable of direct reducing fullerenes in the presence of coordinating ligands.[7,8] The most part of metal porphyrins (M = Zn, Mn, Co, Fe) have weak donor properties toward fullerenes and form only molecular complexes with the latter.[9—11] Such metal porphyrins can be involved in ionic complexes with fullerenes $(Cat^+) \cdot (C_{60}{}^{\bullet -})$ due to the formation of coordination bonds between the metal porphyrin and nitrogen-containing cation (Cat^+)[12—17] or due to coordination bonds M(metal porphyrin)—C($C_{60}{}^-$) with the fullerene anion.[18—20] In the first case, positively charged coordination structures $(Cat^+)_n \cdot (M^{II}Porph)$ (Porph is porphyrin, $n = 1$ or 2) are formed in solution. They interact with fullerene radical anions or dianions to form multicomponent ionic complexes $\{(Cat^+)_n \cdot (M^{II}Porph)\} \cdot (C_{60}{}^{n-})$ ($n = 1$ or 2). In the ionic complexes of metal porphyrins with fullerenes, the fullerene anions form various packings and σ-bonded fuller-

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ene structures: one-dimensional chains of $C_{60}{}^{\bullet -}$,[12,13] isolated dianions $C_{60}{}^{2-}$,[14] diamagnetic dimers $(C_{60}{}^-)_2$ and $(C_{70}{}^-)_2$ bound by one C—C bond,[12,15] paramagnetic dimers $(C_{60}{}^-)_2$ bound by two C—C bonds,[16] and diamagnetic coordinately bound structures with cobalt(II) tetraphenyl- and octaethylporphyrinates: $\{Co^{II}TPP \cdot (C_{60}{}^-)\}$,[18,19] $\{Co^{II}OEP \cdot (C_{60}{}^-)\}$,[13,20] and $\{(MDABCO^+) \cdot Co^{II}OEP \cdot (C_{60}{}^-)\}$ (MDABCO is *N*-methyldiazabicyclooctane (4-aza-1-methylazoniabicyclo[2.2.2]octane) cation).[20]

Like metal porphyrins, phthalocyanines represent a large class of macroheterocyclic compounds widely used as dyes and photoactive, magnetic, and conducting materials.[21—23] Phthalocyanines contain a large planar macrocycle, which does not allow them to cocrystallize with neutral spherical fullerenes. In fact, molecular complexes of fullerenes with phthalocyanines have not been obtained so far. Only dyads are known in which phthalocyanines are covalently[24] or coordinately[25] bound to fullerenes. Coordination dyads are formed with fullerenes including nitrogen-containing substituents: pyridine or imidazole.[25]

In this work, we synthesized for the first time the ionic complexes of fullerenes with metal phthalocyanines. The methods for synthesis of such complexes are similar to those developed by us earlier for ionic fullerene complexes with metal porphyrinates. However, it turned out that the formation of the ionic fullerene complexes with phthalocyanines follows quite different scheme. Metal porphyrins coordinate nitrogen-containing cations to form positively charged coordination structures $\{(Cat^+)_n \cdot (M^{II}Porph)\}$ giving multicomponent ionic complexes with $C_{60}{}^{n-}$ ($n = 1$ or 2). Unlike this, negatively charged ligands coordinate to the metal of phthalocyanines, and the ionic compound of phthalocyanine and fullerene is formed as a binary salt containing two different anions $\{M^{II}Pc(An^-)\} \cdot (C_{60}{}^{\bullet -}) \cdot (Cat^+)_2$. Compounds $\{Mn^{II}Pc(EtS^-)_x \cdot (I^-)_{1-x}\} \cdot (C_{60}{}^{\bullet -}) \cdot (PMDAE^+)_2 \cdot C_6H_4Cl_2$ (PMDAE is *N*,*N*,*N*′,*N*′,*N*′-pentamethyldiaminoethane, $x = 0.87$, **1**) and $\{Zn^{II}Pc(EtS^-)_y \cdot (I^-)_{1-y}\}_2 \cdot (C_{60}{}^-)_2 \cdot (PMDAE^+)_4 \cdot (C_6H_4Cl_2)$ ($y = 0.5$, **2**) (Fig. 1) were obtained as single crystals, which made it possible to study their crystal structures. Specific features of the packings of the spherical fullerene molecules with the planar phthalocyanine molecules and coordination of the iodide and ethanethiolate anions to the metal phthalocyanines were considered.

Experimental

Manganese(II) and zinc(II) phthalocyanines, sodium ethanethiolate, *N*,*N*,*N*′,*N*′-tetramethyldiaminoethane, and methyl iodide were purchased from Aldrich. Fullerene C_{60} (purity 99.9%) was used. Solvents were purified by distillation in argon. *o*-Dichlorobenzene was distilled with CaH_2 *in vacuo*, benzonitrile was distilled over sodium *in vacuo*, and hexane was distilled over Na/benzophenone. Prior to use the solvents were degassed and stored in a box with an inert atmosphere. All procedures on the preparation of solutions and crystal growth were carried out in a box with an inert atmosphere (MBraun 150B-G) and oxygen and water contents lower than 1 ppm. Pellets in KBr for IR spectra were also prepared in the box.

Synthesis of the compounds. *N*,*N*,*N*′,*N*′,*N*′-Pentamethyldiaminoethane iodide (PMDAE • I) was obtained by the addition of MeI (0.75 mL, 0.012 mmol) to a solution of TMDAE (2 mL, 0.013 mmol) in acetonitrile (10 mL) with stirring. After

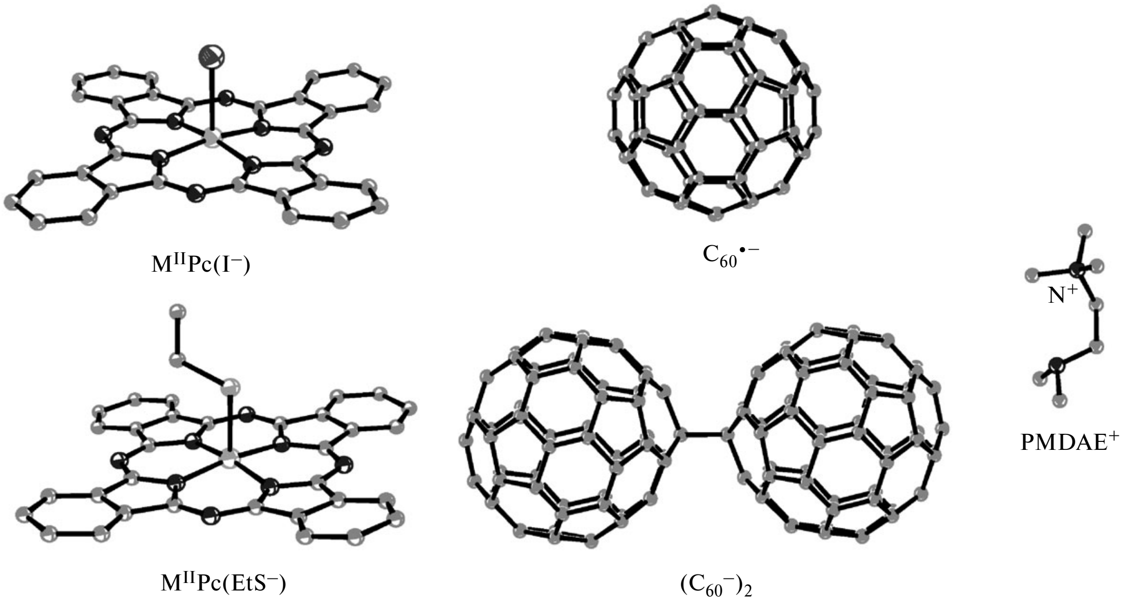

Fig. 1. Molecular structures of the components of the complexes $\{Mn^{II}Pc(EtS^-)_x \cdot (I^-)_{1-x}\} \cdot (C_{60}{}^{\bullet -}) \cdot (PMDAE^+)_2 \cdot C_6H_4Cl_2$ ($x = 0.87$, **1**) and $\{Zn^{II}Pc(EtS^-)_y \cdot (I^-)_{1-y}\}_2 \cdot (C_{60}{}^-)_2 \cdot (PMDAE^+)_4 \cdot (C_6H_4Cl_2)$ ($y = 0.5$, **2**). Manganese(II) and zinc(II) phthalocyanines coordinate ethanethiolate and iodide anions in ratios of 0.87 : 0.13 (**1**) and 0.50 : 0.50 (**2**).

MeI was added, the solution was stirred for 2 h and then placed in a refrigerator at −24 °C for ~14 h. White crystals of PMDAE • I were filtered off, washed with ether, and dried in air. The yield of the salt was 1.3 g (40%).

The crystals of complex $\{Mn^{II}Pc(EtS^-)_x \cdot (I^-)_{1-x}\} \cdot (C_{60}^{\cdot -}) \cdot (PMDAE^+)_2 \cdot C_6H_4Cl_2$ ($x = 0.87$, **1**) were obtained by the diffusion method. Fullerene C_{60} (30 mg, 0.042 mmol), fresh sodium ethanethiolate (30 mg, 0.36 mmol), an excess of PMDAE • I (100 mg, 0.175 mmol), and $Mn^{II}Pc$ (24 mg, 0.042 mmol) were stirred in 14 mL of a $C_6H_4Cl_2$—C_6H_5CN (6 : 1) mixture for 4 h at 60 °C. On stirring the solution turned saturated blue, and phthalocyanine and fullerene were completely dissolved. The solution was cooled to ~20 °C and filtered into a 50-mL glass tube with the ground-in stopper. Hexane (26 mL) was layered onto the obtained solution. Diffusion was carried out for 1 month, after which the solvent was poured down and the crystals formed on the tube walls were collected and washed with hexane. It is seen in a microscope that the mixture consists of crystals of two phases different in shape. The first phase represents black triangular prisms with copper luster characteristic of phthalocyanines (50% yield). The crystals were selected by the shape using a microscope, and the selected testing of these crystals in X-ray diffraction showed that all of them belonged to the same phase. The composition of the crystals $\{Mn^{II}Pc(EtS^-)_x \cdot (I^-)_{1-x}\} \cdot (C_{60}^{\cdot -}) \cdot (PMDAE^+)_2 \cdot C_6H_4Cl_2$ ($x = 0.87$, **1**) was established by X-ray diffraction data and confirmed by microprobe X-ray analysis using a SUPRA-50UP electron microscope. The obtained ratio of heavy elements in the crystals (Mn : I : S : Cl = = 1.00 : 0.22 : 0.84 : 2.10) is rather close to that calculated for the composition determined using X-ray diffraction on a single crystal (1.00 : 0.13 : 0.87 : 2.00). The crystals of the second phase are black elongated prisms with the square cross-section with characteristic copper luster. They were obtained in a lower yield of 30%. The selected testing of the single crystals by X-ray diffraction showed that they belonged to another phase and by the crystal cell parameters were isostructural to the crystals of complex **2** described further.

The crystals of the ionic fullerene complex with zinc(II) phthalocyanine (**2**) were synthesized similarly using $Zn^{II}Pc$. The crystals of two types were obtained: triangular prisms and elongated prisms with the square cross-section. The X-ray diffraction analysis showed that the crystals in the form of triangular prisms were isostructural to the crystals of complex **1**. The full X-ray diffraction analysis was carried out for the elongated prisms of square cross-section and their composition was established to be $\{Zn^{II}Pc(EtS^-)_y \cdot (I^-)_{1-y}\}_2 \cdot (C_{60}^-)_2 \cdot (PMDAE^+)_4 \cdot (C_6H_4Cl_2)$ ($y = 0.5$, **2**).

X-ray diffraction analysis. The X-ray diffraction data for crystals **1** and **2** were collected on an Oxford Diffraction Gemini-R diffractometer with a CCD detector (Mo-Kα radiation, λ = 0.71073 Å) equipped with an Oxford Instruments Cryojet System cryostat. The data were collected using φ and ω scan modes with an frame width of 0.3° and a storage of 30 s per frame. The data were integrated, sorted out, and averaged using the CrysAlisPro program package (Oxford Diffraction Ltd.). The structure was solved by a direct method and refined by least squares on F^2 using the SHELX-97 program.[26] All non-hydrogen atoms were refined in the anisotropic approximation. The positions of hydrogen atoms were calculated geometrically. Selected crystallographic data, including the numbers in the Cambridge Crystallographic Data Centre for **1** and **2**, are given in Table 1.

Table 1. Selected crystallographic data for complexes **1** and **2**

Parameter	1	2
Empirical formula	$C_{113.74}H_{62.35}Cl_2I_{0.13}MnN_{12}S_{0.87}$	$C_{220}H_{117}Cl_2IN_{24}SZn_2$
M	1767.22	3456.98
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	13.1279(4)	22.1805(19)
b/Å	16.3136(5)	15.6157(8)
c/Å	20.2040(6)	24.013(2)
α/deg	112.581(3)	90.00
β/deg	92.136(3)	116.140(11)
γ/deg	104.376(3)	90.00
V/Å^3	3827.4(2)	7466.7(10)
Z	2	2
d_{calc}/g cm^{-3}	1.533	1.538
μ/mm^{-1}	0.388	0.654
F(000)	1817	3536
T_{exp}/K	110(2)	120(2)
$2\theta_{max}$/deg	57.4	55.76
Number of reflections	47397	52746
Number of independent reflections	19683	17190
Number of parameters/restraints	1839/1011	1709/1567
Number of reflections with $F > 2\sigma(F)$	17421	11340
R Factor $[F > 2\sigma(F)]$	0.0455	0.0743
wR	0.1192	0.1835
GOF	1.002	1.024
CCDC No.	800158	811700

Disorder in the structures of complexes 1 and 2. The structures of complexes **1** and **2** are characterized by structural disorder, which is rather often observed in the neutral and ionic fullerene complexes.[11,13,19] In complex **1**, the radical anion $C_{60}{}^{\bullet -}$ is disordered between two orientations with occupancies of 0.687(2)/0.313(2). One of the two cations $PMDAE^+$ is disordered over three positions with the 0.55/0.25/0.20 occupancy. The solvent molecule $C_6H_4Cl_2$ is disordered over two positions with the 0.55/0.45 occupancies. In the structure of complex **2** , the radical anions $C_{60}{}^{\bullet -}$ dimerize to form the dimer $(C_{60}{}^{-})_2$ bound by one C—C bond. The dimers are disordered with one main orientation having the 0.85 occupancy, whereas the second orientation has an orientation of 0.15 only. The both $PMDAE^+$ cations in complex **2** are disordered over two orientations with 0.50/0.50 and 0.70/0.30 occupancies. Only orientations with the maximum occupancies are shown for all disordered components in Figs 1—4. Intermolecular distances were also estimated for the components with the maximum occupancy.

A certain structural disorder is observed for the coordination of the anions with metal phthalocyanines, because the iodide and ethanethiolate anions coordinate to the metal in different ratios. For complexes **1** and **2**, these ratios are 0.87/0.13 and 0.50/0.50, respectively. Only one coordination structure with the iodide anion $\{M^{II}Pc \cdot (I^-)\}$ is shown in Figs 2—4.

Results and Discussion

We have earlier developed the universal method for the synthesis of ionic fullerene compounds with various organic cations. The method is based on the reduction of fullerene with an excess of sodium thiolate in a $C_6H_4Cl_2$—C_6H_5CN (6 : 1) mixture in the presence of salts of organic cations $(Cat^+) \cdot (I^-)$, where the sodium cation is exchanged for an organic cation in the cationic metathesis reaction. Excessive ethanethiolate and sodium iodide are poorly soluble in the used mixture of solvents and can be filtered off. Under these conditions, fullerene is reduced only to the radical anion state. Salt $(Cat^+) \cdot (C_{60}{}^{\bullet -})$ that formed as crystals is precipitated by hexane diffusion.[27,28] The addition of metal porphyrinate to the reaction mixture makes it possible to obtain a wide range of ionic multicomponent complexes $(Cat_1{}^+)_n \cdot (M^{II}Porph)$ ($n = 1$ or 2).[12—20]

In the present work, the fullerene complexes with phthalocyanines were synthesized by a similar reaction using manganese(II) and zinc(II) phthalocyanines capable of extracoordinating. The organic cation used was $PMDAE^+$, whose one nitrogen atom can potentially participate in coordination with metal phthalocyanines. During the reduction of fullerene, phthalocyanines are completely dissolved to form an intensely blue-colored solution. The diffusion of hexane into this solution results in the formation of crystals of two types of different shapes. For both manganese(II) and zinc(II) phthalocyanines, the crystals were obtained as triangular and elongated prisms of square cross-section; and the crystals of the same morphology are isostructural. The structure and composition of the triangular prisms were established for the complex with manganese(II) phthalocyanine $\{Mn^{II}Pc \cdot (EtS^-)_x \cdot (I^-)_{1-x}\} \cdot (C_{60}{}^{\bullet -}) \cdot (PMDAE^+)_2 \cdot C_6H_4Cl_2$ ($x = 0.87$, **1**). The structure of the elongated prisms of square cross-section was determined for the complex with zinc(II) phthalocyanine $\{Zn^{II}Pc(EtS^-)_y \cdot (I^-)_{1-y}\}_2 \cdot (C_{60}{}^{-})_2 \cdot (PMDAE^+)_4 \cdot (C_6H_4Cl_2)$ ($y = 0.5$, **2**).

It has earlier been shown that the reduction of fullerene with sodium ethanethiolate in a $C_6H_4Cl_2$—C_6H_5CN (6 : 1)

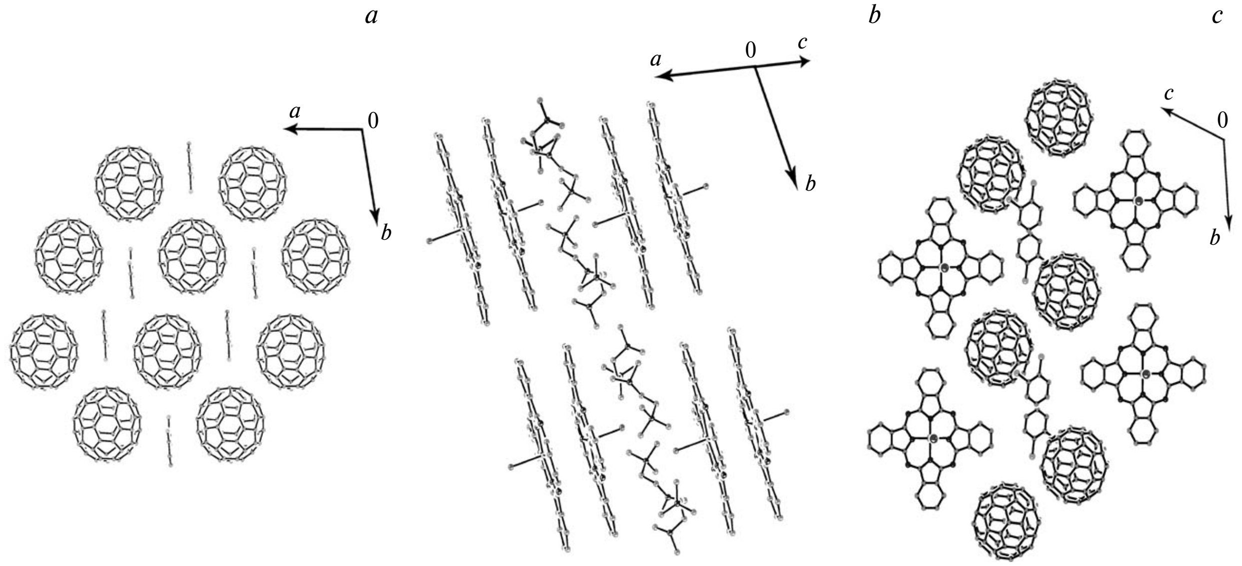

Fig. 2. Crystal structure of complex **1**. The view along the axis *c* on the fullerene layers (*a*); the view on the phthalocyanine layers containing the cations $PMDAE^+$ (*b*); and the view along the fullerene and phthalocyanine layers (along the axis *a*), indicating the interplay between the layers (*c*).

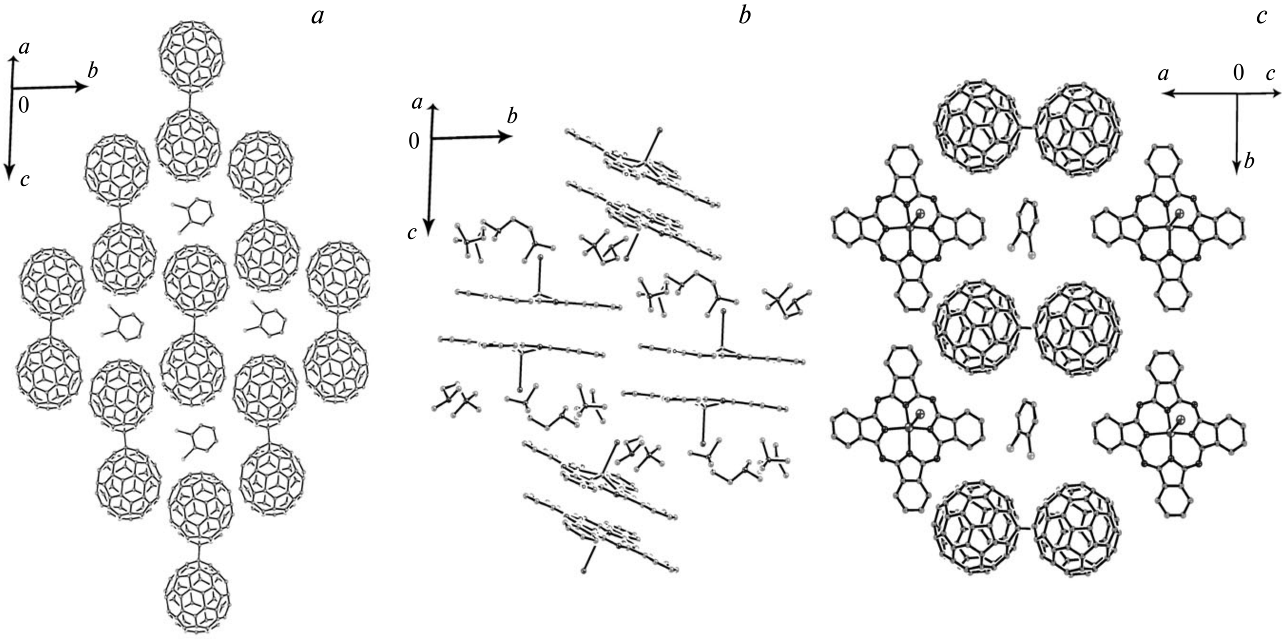

Fig. 3. Crystal structure of complex **2**. The view on the fullerene layers (*a*); the view on the fullerene layers containing the cations $PMDAE^+$ (*b*); and the view along the fullerene and phthalocyanine layers, indicating the interplay between the layers (*c*).

mixture of solvents affords only fullerene radical anions, while no dianions are formed. Phthalocyanines have substantially more negative reduction potentials ($E_{red}{}^{0/-}$ = −0.69 V for $Mn^{II}Pc$ and $E_{red}{}^{0/-}$ = −0.86 V for $Zn^{II}Pc$)[**29,30**] than the first reduction potential of fullerene C_{60} ($E_{red}{}^{0/-}$ = −0.44 V)[**31**] and cannot be reduced during

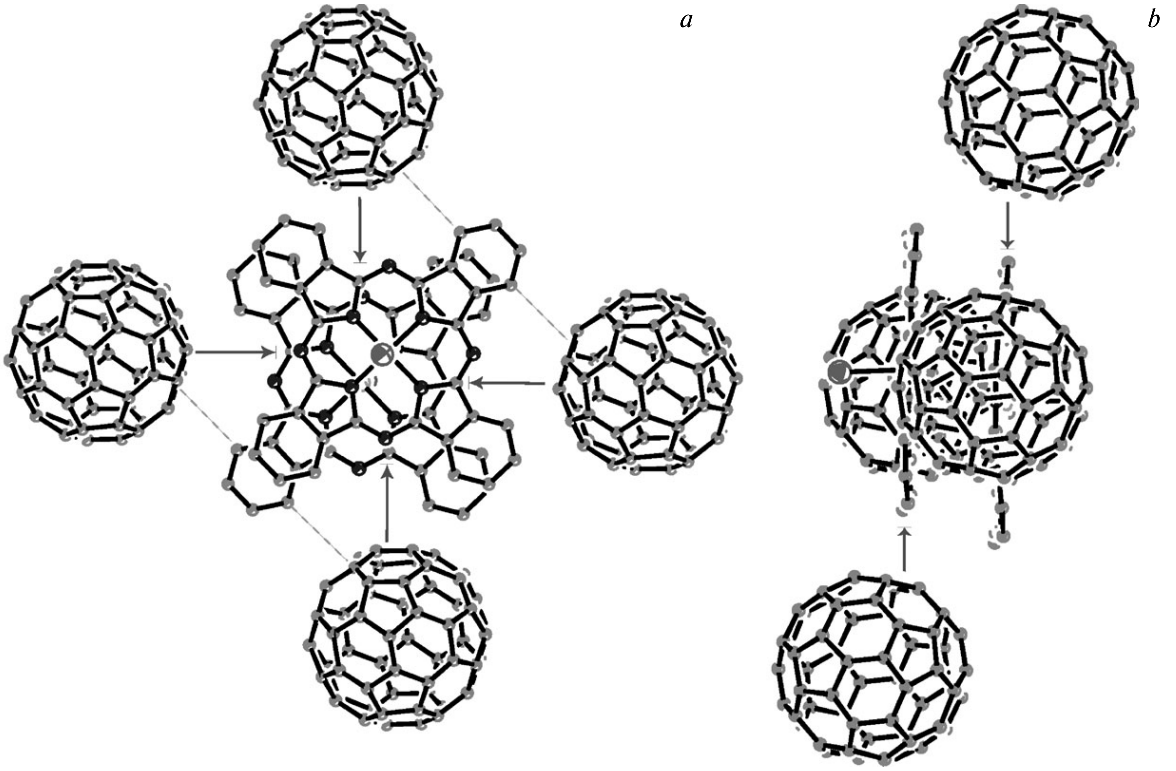

Fig. 4. Environment of the dimer $\{Mn^{II}Pc(An^-)\}_2$ of four radical anions $C_{60}{}^{\bullet-}$ in the crystal structure of **1**. Arrows show directions from fullerene to the nearest imine nitrogen atom of phthalocyanine.

fullerene reduction. Phthalocyanines themselves are almost insoluble in a $C_6H_4Cl_2$—PhCN mixture. However, since the reaction mixture include different anions (EtS^- and I^-, and the iodide anions are produced by organic salt PMDAE • I, whereas the ethanethiolate anions are present in the reducing agent EtSNa), phthalocyanines form negatively charged coordination structures $M^{II}Pc \cdot (An^-)$, which results, most likely, to the dissolution of phthalocyanines during fullerene reduction. The cations $PMDAE^+$ can also coordinate to the metal atom of phthalocyanines ($M^{II}Pc$) to form positively charged coordination structures $M^{II}Pc \cdot (PMDAE^+)_n$ (n = 1 or 2). However, these positively charged structures do not form ionic complexes with $C_{60}{}^{\cdot -}$.[12—20] In spite of the variety of ionic structures of metal porphyrins with fullerenes, no case is known where the iodide or ethanethiolate anion would coordinate to metal porphyrin. This is the main distinction of metal phthalocyanines from metal porphyrins.

In compounds **1** and **2**, two $PMDAE^+$ cations fall on one coordination species $M^{II}Pc(An^-)$ and one molecule of fullerene C_{60}. Fullerene has one negative charge, and the negative charge of $M^{II}Pc(An^-)$ is concentrated on the ligand anion, due to which metal phthalocyanines remain uncharged. This is related to the fact that manganese(II) and zinc(II) phthalocyanines are reduced to substantially more negative potentials than fullerenes. It follows from the consideration of the redox potentials ($Mn^{II}Pc$ is oxidized at –0.08 V and is reduced at –0.69 V,[29] $Zn^{II}Pc$ is oxidized at +0.67 V and is reduced at –0.86 V,[30] C_{60} is reduced at –0.44 V, and the dianion is formed at –0.82 V (see Ref. 31)) that $C_{60}{}^-$ can coexist only with neutral phthalocyanine $M^{II}Pc$. Other combinations of the charge distribution, for instance, $\{Mn^{III}Pc(An)\}$ and $C_{60}{}^{2-}$ or $\{M^{I}Pc(An)\}^{2-}$ and neutral C_{60} are unstable.

The data of IR spectroscopy for complexes **1** and **2** and the formation of dimers $(C_{60}{}^-)_2$ bound by one C—C bond in complex **2** also indicate the radical anion state of fullerenes in these complexes.

Crystal structures of compounds 1 and 2. Complex **1** has a layered structure. Fullerenes form honeycomb-like layers with large cavities, whose size is enough to incorporate two solvent molecules $C_6H_4Cl_2$ (see Fig. 2, *a*). Numerous van der Waals contacts C...C and Cl...C appear between the solvent and fullerene. Each fullerene molecule has three adjacent fullerenes with center-to-center distances of 10.13, 10.16, and 10.29 Å. These distances are near to the van der Waals diameter of the C_{60} molecule (10.18 Å). No dimerization of $C_{60}{}^{\cdot -}$ is observed in complex **1** down to 110(2) K because of rather long distances between the radical anions $C_{60}{}^{\cdot -}$, although $C_{60}{}^{\cdot -}$ is strongly prone to dimerization.[15,27,37—41]

Note that honeycomb-like fullerene layers with three neighbors for each fullerene are also formed in the crystal structure of complex **2**; however, cavities in the layer are substantially smaller and can incorporate only one $C_6H_4Cl_2$ molecule (see Fig. 3, *a*). The smaller cavities result in the situation that the distances between the fullerene anions in the layer decrease. Two adjacent fullerenes have center-to-center distances of 9.90 and 10.11 Å and shortened van der Waals C...C contacts (3.39 Å) are formed between them. The distances with the third neighbor in the direction of the crystallographic axis *c* are so short that the radical anions $C_{60}{}^{\cdot -}$ are dimerized in this direction to form dimers $(C_{60}{}^-)_2$ bound by one C—C bond. The distance between the centers of fullerenes in the dimers $(C_{60}{}^-)_2$ in complex **2** is 9.27 Å and the C—C bond length between the fullerenes is 1.594(7) Å, which is characteristic of dimers $(C_{60}{}^-)_2$ of this type.[15,27,37—41] It was shown for many examples that the dimers $(C_{60}{}^-)_2$ bound by one C—C bond are diamagnetic.[15,27,37—41]

In complexes **1** and **2**, the coordination structures $M^{II}Pc(An^-)$ are packed into dimers $\{M^{II}Pc(An^-)\}_2$ with the parallel arrangement of the phthalocyanine planes and short interplanar distances (see Figs 2, *b* and 3, *b*). The contacts between the planes passed through eight nitrogen atoms of the phthalocyanine cycle are 3.14 Å for $\{Mn^{II}Pc(An^-)\}_2$ and 3.27 Å for $\{Zn^{II}Pc(An^-)\}_2$. The short interplanar contacts result in the formation of numerous van der Waals contacts between two phthalocyanines in the dimer. The phthalocyanine dimers and cations $PMDAE^+$ lie between the fullerene layers and their packing can also be considered as a layer in which the phthalocyanine chains along the crystallographic axis *b* alternate with the chains of the cations (see Figs 2, *b* and 3, *b*). The phthalocyanine dimers in the chains of complexes **1** and **2** are arranged in different manner. In the first case, all phthalocyanine planes are parallel to each other (see Fig. 2, *b*), whereas in the second case, the phthalocyanine planes in the adjacent chains are not parallel (see Fig. 3, *b*). Although phthalocyanines form chains, there are not short van der Waals contacts between them (for the both complexes, the closest contact C...C exceeds 3.6 Å). The cations $PMDAE^+$ are oriented in the layer in such a way that the positively charged groups $—N^+Me_3$ are close to the negatively charged iodine and sulfur atoms in the coordination structures $M^{II}Pc(An^-)$ (see Figs 2, *b* and 3, *b*).

The negatively charged layers of fullerenes and phthalocyanines are retained together by the cations $PMDAE^+$. The honeycomb-like layers of fullerenes include large vacancies incorporated in part the phenylene substituents from two phthalocyanines composing the dimer $\{M^{II}Pc(An^-)\}_2$. As a result, each pair of fullerenes or the dimer $(C_{60}{}^-)_2$ are surrounded in the structure by four phthalocyanines (see Figs 2, *c* and 3, *c*) and, on the contrary, each phthalocyanine dimer $\{M^{II}Pc(An^-)\}_2$ is surrounded by four anions of fullerenes (see Fig. 4, *a*). of these four fullerenes, two fullerenes are arranged closer to one phthalocyanine of the dimer $\{M^{II}Pc(An^-)\}_2$ and two fullerenes are closer to another phthalocyanine (see Fig. 4, *b*). Thus, the packing of spherical fullerene molecules and planar phthalocyanine molecules in crystal is achieved due to the insertion of large fullerene molecules between two phenylene groups of phthalocyanine in front of its imine nitrogen atom. Fullerenes form several somewhat shortened van der Waals contacts C...C with the phenylene groups of phthalocyanine in the range 3.371—3.388 Å (they are shown by dashed lines in Fig. 4, *a*). The earlier studied ionic complexes of porphyrins and fullerenes are characterized by strong π—π-interactions of the porphyrin macrocycle with five- and six-membered cycles of fullerenes.[11—20] These interactions are not observed for ionic complexes **1** and **2**. This is related to the fact that for phthalocyanine the π—π-interaction with the adjacent phthalocyanine molecule becomes more advantageous, which results in the formation of the dimer $\{M^{II}Pc(An^-)\}_2$.

Specific features of coordination of anions with metal phthalocyanines. Let us consider specific features of coordination of the anions EtS^- and I^- with metal phthalocyanines (see Fig. 1). The Mn—S and Mn—I bond lengths in the coordination structures $Mn^{II}Pc(EtS^-)$ and $Mn^{II}Pc(I^-)$ in complex **1** are 2.5217(8) and 2.8415(13) Å, respectively. The manganese(II) atom has only one position for the both structure, and no noticeable elongation of the ellipsoid of the manganese(II) atom is observed. The averaged length of the equatorial bonds Mn—N(Pc) is 1.9488(13) Å, whereas the shift of the manganese(II) atom from the plane of four nitrogen atoms of the phthalocyanine cycle is only 0.173(2) Å. The geometry of the coordination structures $Mn^{II}Pc(EtS^-)$ and $Mn^{II}Pc(I^-)$ was determined for the first time. Only one compound $Mn^{III}PcI \cdot (I_2)_{0.5}$, in which manganese(III) phthalocyanine coordinates the iodide anion was described previously.[32] This compound was synthesized by the reaction of the manganese salt with phthalonitrile in the presence of iodine vapor. In this compound the Mn—I bond length is 2.731(2) Å, the averaged length of the equatorial Mn—N(Pc) bond is 1.966(2) Å, and the shift of the manganese atom from the plane of four nitrogen atoms is 0.261(2) Å. It should be mentioned that the geometry of the coordination structures $Mn^{II}Pc \cdot L$ with the pentacoordinate manganese(II) atom differs substantially from the geometry of analogous coordination structures with manganese(II) tetraphenylporphyrinate $Mn^{II}TPP \cdot L$ in which the average equatorial bonds Mn—N(Pc) are noticeably longer (2.0008—2.0012 Å) and the shift of the manganese atom from the porphyrin plane is substantially greater (0.40—0.56 Å) due to the high-spin state of manganese ($S = 5/2$).[13,15,33—35] It is shown[36] that the shorter equatorial bonds Mn—N(Pc) in the structures $Mn^{II}Pc \cdot L$ are related to the intermediate spin state of manganese(II) ($S = 3/2$).

The coordination structures $Zn^{II}Pc(EtS^-)$ and $Zn^{II}Pc(I^-)$ in complex **2** differ noticeably from analogous structures with $Mn^{II}Pc$. The zinc(II) atom also has only one position in the both coordination structures. The Zn—S and Zn—I bonds are substantially shorter (2.379(5) and 2.703(3) Å, respectively). This results in the elongation of the average equatorial bonds Zn—N(Pc) in the phthalocyanine molecule to 2.037(3) Å and the shift of the zinc(II) atom from the plane of four nitrogen atoms of the phthalocyanine cycle by 0.510(2) Å, which is noticeably larger than that for $Mn^{II}Pc$.

Thus, in this work we synthesized for the first time ionic compounds **1** and **2** containing the fullerene anions and coordination structures of manganese(II) and zinc(II) phthalocyanines with the anions I^- and EtS^-. These structures are formed upon the coordination of the iodide or ethanethiolate anions to the metal of phthalocyanine $\{M^{II}Pc(An^-)\}$, but the phthalocyanines themselves remain, most likely, uncharged. In these compounds, fullerenes exist in the radical anion state (**1**) or form dimers $(C_{60}^-)_2$ bound by one C—C bond (**2**). As a result, these compounds can be presented as binary salts containing two types of anions $\{M^{II}Pc(An^-)\} \cdot (C_{60}^{\cdot -}) \cdot (PMDAE^+)_2$. The both types of anions form layers retained together by the cations. The packings of molecules with different shapes is achieved by the insertion of large fullerene molecules between the phenylene groups of the planar phthalocyanine molecules. As a whole, the ionic complexes of fullerenes with phthalocyanines strongly differ from the earlier studied ionic complexes of fullerenes with metal porphyrinates. Metal porphyrinates (M = Zn, Mn, Co, Fe) are characterized by the formation of positively charged coordination structures $(D_1^+)_n \cdot M^{II}Porph$ ($n = 1$ or 2), which compose ionic complexes with the radical anions or dianions of fullerenes. On the contrary, metal phthalocyanines coordinate negatively charged ligands and the ionic compounds with fullerenes are formed as binary salts. The π—π-interactions between the porphyrin macrocycle and five- or six-membered cycles of fullerenes represent another specific feature of the ionic fullerene compounds with metal porphyrinates. No these interactions are observed in the case of phthalocyanines and instead the dimers $\{M^{II}Pc(An^-)\}_2$ with the strong π—π-interaction between two phthalocyanine planes are formed.

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References

1. D. M. Guldi, *Chem. Soc. Rev.*, 2002, **31**, 22.
2. S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hadju, R. Bible, M. M. Olmstead, K. Maitra, A. J. Fisher, A. L. Balch, H. C. Dorn, *Nature*, 1999, **401**, 55.
3. M. M. Olmstead, A. de Bettencourt-Dias, S. Stevenson, H. C. Dorn, A. L. Balch, *J. Am. Chem. Soc.*, 2002, **124**, 4172.
4. L. Epple, K. Amsharov, K. Simeonov, I. Dix, M. Jansen, *Chem. Commun.*, 2008, 5610.

5. M. Zheng, F. Li, Z. Shi, Y. Gao, K. M. Kadish, *J. Org. Chem.*, 2007, **72**, 2538.
6. G. Saito, J. P. Ferraris, *Bull. Chem. Soc. Jpn*, 1980, **53**, 2141.
7. A. Pénicaud, J. Hsu, C. A. Reed, A. Koch, K. C. Khemani, P.-M. Allemand, F. Wudl, *J. Am. Chem. Soc.*, 1991, **113**, 6698.
8. J. Stinchcombe, A. Pénicaud, P. Bhyrappa, P. D. W. Boyd, C. A. Reed, *J. Am. Chem. Soc.*, 1993, **115**, 5212.
9. M. M. Olmstead, D. A. Costa, K. Maitra, B. C. Noll, S. L. Phillips, P. M. Van Calcar, A. L. Balch, *J. Am. Chem. Soc.*, 1999, **121**, 7090.
10. E. I. Yudanova, D. V. Konarev, R. N. Lyubovskaya, L. L. Gumanov, *Izv. Akad. Nauk*, *Ser. Khim.*, 1999, 722 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1999, **48**, 718].
11. D. V. Konarev, I. S. Neretin, Yu. L. Slovokhotov, E. I. Yudanova, N. V. Drichko, Yu. M. Shul´ga, B. P. Tarasov, L. L. Gumanov, A. S. Batsanov, J. A. K. Howard, R. N. Lyubovskaya, *Chem. Eur. J.*, 2001, **7**, 2605.
12. D. V. Konarev, S. S. Khasanov, A. Otsuka, G. Saito, R. N. Lyubovskaya, *Inorg. Chem.*, 2007, **46**, 2261.
13. D. V. Konarev, S. S. Khasanov, G. Saito, R. N. Lyubovskaya, *Cryst. Growth Des.*, 2009, **9**, 1170.
14. D. V. Konarev, S. S. Khasanov, G. Saito, R. N. Lyubovskaya, *J. Porph. Phth.*, 2008, **12**, 1146.
15. D. V. Konarev, S. S. Khasanov, G. R. Mukhamadieva, L. V. Zorina, A. Otsuka, H. Yamochi, R. N. Lyubovskaya, *Inorg. Chem.*, 2010, **49**, 3881.
16. D. V. Konarev, S. S. Khasanov, A. Otsuka, G. Saito, R. N. Lyubovskaya, *J. Am. Chem. Soc.*, 2006, **128**, 9292.
17. D. V. Konarev, R. N. Lyubovskaya, *Macroheterocycles*, 2009, **2**, 191.
18. D. V. Konarev, S. S. Khasanov, A. Otsuka, Y. Yoshida, R. N. Lyubovskaya, G. Saito, *Chem. Eur. J.*, 2003, **9**, 3837.
19. D. V. Konarev, S. S. Khasanov, A. Otsuka, G. Saito, R. N. Lyubovskaya, *Dalton Trans.*, 2009, 6416.
20. D. V. Konarev, S. S. Khasanov, A. Otsuka, G. Saito, R. N. Lyubovskaya, *Chem. Eur. J.*, 2006, **12**, 5225.
21. T. Nyokong, *Coord. Chem. Rev.*, 2007, **251**, 1707.
22. T. Inabe, H. Tajima, *Chem. Rev.*, 2004, **104**, 5503.
23. D. K. Rittenberg, L. Baars-Hibbe, A. B. Böhm, J. S. Miller, *J. Mater. Chem.*, 2000, **10**, 241.
24. G. Bottari, T. Torres, *Macroheterocycles*, 2010, **3**, 16.
25. M. E. El-Khouly, O. Ito, P. M. Smith, F. D´Souza, *J. Photochem. Photobiol. C: Photochem. Rev.*, 2004, **5**, 79.
26. G. M. Sheldrick, *SHELX97*, University of Göttingen, Göttingen, Germany, 1997.
27. D. V. Konarev, S. S. Khasanov, G. Saito, A. Otsuka, R. N. Lyubovskaya, *J. Mater. Chem.*, 2007, **17**, 4171.
28. D. V. Konarev, S. S. Khasanov, A. Otsuka, M. Maesato, G. Saito, R. N. Lyubovskaya, *Angew. Chem.*, 2010, **49**, 4829.
29. A. B. P. Lever, P. C. Minor, J. P. Wilshire, *Inorg. Chem.*, 1981, **20**, 2550.
30. A. Giraudeau, A. Louati, M. Gross, J. J. Andre, J. Simon, C. H. Su, K. M. Kadish, *J. Am. Chem. Soc.*, 1983, **105**, 2917.
31. D. Dubois, K. M. Kadish, S. Flanagan, R. F. Haufler, L. P. F. Chibante, L. J. Wilson, *J. Am. Chem. Soc.*, 1991, **113**, 4364.
32. J. Janczak, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2004, **60**, m330-m332.
33. J. F. Kirner, C. A. Reed, W. R. Scheidt, *J. Am. Chem. Soc.*, 1977, **99**, 2557.
34. D. V. Konarev, S. S. Khasanov, G. Saito, A. Otsuka, R. N. Lyubovskaya, *Inorg. Chem.*, 2007, **46**, 7601.
35. D. V. Konarev, S. S. Khasanov, R. N. Lyubovskaya, *Cryst. Growth Des.*, 2010, **10**, 1451.
36. J. F. Kirner, W. Dow, W. R. Scheidt, *Inorg. Chem.*, 1976, **15**, 1685.
37. D. V. Konarev, S. S. Khasanov, A. Otsuka, G. Saito, *J. Am. Chem. Soc.*, 2002, **124**, 8520.
38. D. V. Konarev, S. S. Khasanov, G. Saito, A. Otsuka, Y. Yoshida, R. N. Lyubovskaya, *J. Am. Chem. Soc.*, 2003, **125**, 10074.
39. G. A. Domracheev, Yu. A. Shevelev, V. K. Cherkasov, G. V. Markin, G. K. Fukin, S. Ya. Khorshev, B. S. Kaverin, V. L. Karnatsevich, *Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 1973 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2056].
40. D. V. Konarev, S. S. Khasanov, A. Y. Kovalevsky, G. Saito, A. Otsuka, R. N. Lyubovskaya, *Dalton Trans.*, 2006, 3716.
41. D. V. Konarev, S. S. Khasanov, R. N. Lyubovskaya, *Izv. Akad. Nauk*, *Ser. Khim.*, 2007, 361 [*Russ. Chem. Bull.*, *Int. Ed.*, 2007, **56**, 371].

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